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(54) Title: LUBRICATING OIL COMPOSITION COMPRISING AN ADDITIVE COMBINATION OF A CARBOXYLIC ACID AND AN AMINE AS ANT-RUST AGENT

(57) Abstract: Lubricating oil composition comprising a minor amount of an additive combination comprising (i) a carboxylic acid-based or carboxylic acid ester based anti-rust agent; (ii) at least one type of amine selected from among the group comprising (A) the alkyl amines which can be represented by general formula (1) $(R^1)_nNH_{3-n}$, wherein R^1 represents a saturated or unsaturated alkyl group which has from 12 to 30 carbon atoms, and n is an integer of value 1 or 2; and (B) the N-alkylpolyalkylenediamines which can be represented by general formula (2) $R^2NH(CH_2)_mNH_2$, wherein R^2 represents a saturated or unsaturated alkyl group which has from 12 to 30 carbon atoms, and m is an integer of value from 2 to 5; and a major amount of lubricating oil base oil.



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LUBRICATING OIL COMPOSITION COMPRISING AN ADDITIVE COMBINATION OF A CARBOXYLIC
ACID AND AN AMINE AS ANT-RUST AGENT

The present invention relates to a lubricating oil composition which has excellent anti-rust properties in severe operating environments in which water or seawater is admixed, and which also exhibits excellent properties
5 in terms of both the lubricating properties and anti-corrosion properties in various types of machinery.

Anti-rust agents are added to lubricating oils to protect the mechanical parts from rusting when water or seawater is admixed. In general, anti-rust agents are
10 strongly adsorbed on the metal surface to form a rust-proof film on the metal surface, thus preventing direct contact between the metal and water from occurring and thereby inhibiting the formation of rust.

On the other hand, the wear surfaces of equipment
15 are being subjected to ever more severe conditions as a result of increased running speeds, increased loads and increases in efficiency which have arisen in recent times, and scorching of the wear surfaces is likely to occur as a result of the breakdown of the lubricating oil
20 film.

Consequently, extreme pressure additives, which react with the metal surface and maintain the lubricating properties at the wear surface, are added in suitable amounts to the lubricating oils which are used under such
25 severe conditions in order to prevent sticking of the wear surfaces.

However, it is known that the compounding of an anti-rust agent impedes the reaction between the metal surface and an extreme pressure additive at the wear
30 surface and that the effect of the extreme pressure additive is to a large extent lost as a result.

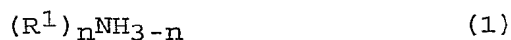
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It is therefore desirable to provide ashless lubricating oil compositions which contain no metal and which, from the viewpoints of the lubrication performance and the anti-rust performance of the lubricating oil, maintain excellent extreme pressure performance even under severe lubrication conditions and at the same time have excellent anti-rust properties.

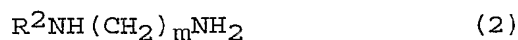
It has now been surprisingly discovered that the amount of anti-rust agent added can be greatly reduced by combining specific alkylamines with the anti-rust agents, with the result that the reduction in the extreme pressure performance caused by the anti-rust agent can be suppressed to a minimum level.

The present invention provides a lubricating oil composition comprising a minor amount of an additive combination comprising

- (i) a carboxylic acid-based or carboxylic acid ester-based anti-rust agent;
- (ii) at least one type of amine selected from among the group comprising (A) the alkyl amines which can be represented by general formula (1),



wherein R^1 represents a saturated or unsaturated alkyl group which has from 12 to 30 carbon atoms, and n is an integer of value 1 or 2; and (B) the N-alkylpolyalkylenediamines which can be represented by general formula (2),



wherein R^2 represents a saturated or unsaturated alkyl group which has from 12 to 30 carbon atoms, and m is an integer of value from 2 to 5; and a major amount of a lubricating oil base oil.

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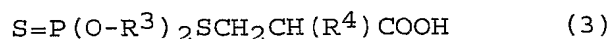
By "major amount" in the present invention is meant at least 50 wt. %, with respect to the total weight of the lubricating oil composition.

Said composition generally comprises from 0.001 to 0.5 part by weight of the carboxylic acid-based or carboxylic acid ester-based anti-rust agent; and from 0.001 to 0.2 part by weight of the at least one type of amine, per 100 parts by weight of lubricating oil base oil.

Preferably, said composition comprises from 0.001 to 0.05 part by weight of the carboxylic acid-based or carboxylic acid ester-based anti-rust agent, per 100 parts by weight of lubricating oil base oil. More preferably, said composition comprises from 0.005 to 0.05 part by weight of said anti-rust agent, per 100 parts by weight of lubricating oil base oil.

Preferably, said composition comprises from 0.001 to 0.05 part by weight of the at least one type of amine, per 100 parts by weight of lubricating oil base oil.

In a further embodiment of the present invention, the lubricating oil composition comprises, as an extreme pressure additive, a β -dithiophosphorylpropionic acid which can be represented by general formula (3),

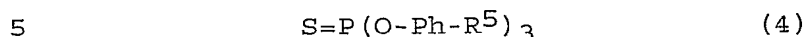


wherein R^3 represents a branched alkyl group which has from 3 to 8 carbon atoms, and R^4 is a hydrogen atom or a group selected from among the linear chain or branched alkyl groups which have from 1 to 4 carbon atoms.

Said extreme pressure additive of formula (3) is preferably present in an amount in the range of from 0.001 to 0.5 part by weight, more preferably from 0.001 to 0.02 part by weight, per 100 parts by weight of lubricating oil base oil.

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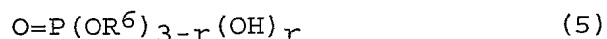
In a still further embodiment of the present invention, the lubricating oil composition comprises, as an extreme pressure additive, a triaryl phosphorothioate which can be represented by general formula (4),



wherein Ph represents a phenyl group, and R^5 is a hydrogen atom or a linear chain or branched alkyl group which has from 1 to 9 carbon atoms.

Said extreme pressure additive of formula (4) is preferably present in an amount in the range of from 0.05 to 5 parts by weight, more preferably from 0.05 to 0.5 part by weight, per 100 parts by weight of lubricating oil base oil.

In another embodiment of the present invention, the lubricating oil composition comprises, as an extreme pressure additive, an acidic phosphate ester which can be represented by general formula (5),



wherein R^6 is a linear chain or branched alkyl group which has from 3 to 13 carbon atoms, and r is an integer of value 1 or 2.

Said extreme pressure additive of formula (5) is preferably present in an amount in the range of from 0.01 to 0.5 part by weight, more preferably from 0.01 to 0.1 part by weight, per 100 parts by weight of lubricating oil base oil.

The lubricating oil composition of the present invention may optionally comprise one or more of compounds of formulae (3) to (5) as extreme pressure additives.

The lubricating oil base oil from which the lubricating oil composition of the present invention is

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constituted is not subject to any particular limitation, provided that it comprises petroleum-based oil and/or synthetic hydrocarbon-based oil.

Lubricating oil base oils having a kinematic
5 viscosity of from 2 to 680 mm²/s (40°C), preferably of from 5 to 320 mm²/s (40°C), and most preferably of from 8 to 220 mm²/s (40°C); a total sulphur content (wt. %) of from 0 to 1 wt. %, and preferably of from 0 to 0.3 wt. %; a total nitrogen content (wt. ppm) of from 0 to 100 ppm,
10 and preferably of from 0 to 30 ppm; and an aniline point of from 80 to 130°C, and preferably of from 100 to 125°C, are preferred.

The petroleum-based lubricating oil base oils which can be used in the present invention may be, for example,
15 individual solvent refined base oils, hydrogenation refined base oils or highly hydrogenated and cracked base oils, or mixtures of such oils. Highly hydrogenated cracked base oils are lubricating oil base oils which have a viscosity index of at least 130 (typically from
20 145 to 155) obtained with a slack wax which has been cracked and solvent de-waxed as the raw material by isomerizing the linear chain paraffins to branched paraffins by hydrogenation cracking in the presence of a catalyst (contact cracking), or lubricating base oils
25 which have a viscosity index of at least 130 (typically from 145 to 155) obtained using heavy linear chain paraffins which have been obtained by Fischer-Tropsch polymerization using the carbon monoxide and hydrogen obtained by a gasification process (partial oxidation) of
30 a natural gas (such as methane) and subjecting this to catalytic cracking and isomerization in the same way as above.

Furthermore, the synthetic hydrocarbon-based base oils which may be used in the present invention include

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the olefin oligomers obtained by the homopolymerization or copolymerization of monomers which have been selected from among the linear chain and branched olefinic hydrocarbons which have from 3 to 15 carbon atoms, and
5 preferably from 4 to 12 carbon atoms.

In the present invention, the petroleum based lubricating oil base oils and synthetic hydrocarbon based base oils can be used individually or in the form of mixtures.

10 The carboxylic acid based or carboxylic acid ester-based anti-rust agents which can be used in the present invention have a carboxylic acid or carboxylic acid ester group in the anti-rust agent molecule and they are widely used generally in lubricating oils.

15 Said anti-rust agents include, for example, monocarboxylic acids which have from 8 to 30 carbon atoms, alkyl or alkenyl succinates or partial esters thereof, hydroxy-fatty acids which have from 12 to 30 carbon atoms and derivatives thereof, sarcosines which
20 have from 8 to 24 carbon atoms and derivatives thereof, amino acids and derivatives thereof, naphthenic acid and derivatives thereof, lanolin fatty acid, mercapto-fatty acids and paraffin oxides.

Particularly preferred anti-rust agents are
25 indicated below.

Examples of Monocarboxylic Acids (C8 - C30)

Caprylic acid, pelargonic acid, decanoic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, behenic acid, cerotic
30 acid, montanic acid, melissic acid, oleic acid, docosanic acid, erucic acid, eicosenic acid, beef tallow fatty acid, soy bean fatty acid, coconut oil fatty acid, linolic acid, linoleic acid, tall oil fatty acid, 12-hydroxystearic acid, laurylsarcosinic acid,
35 myritylsarcosinic acid, palmitylsarcosinic acid,

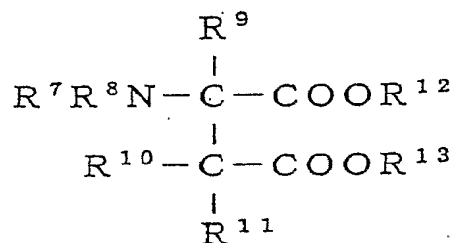
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stearylsarcosinic acid, oleylsarcosinic acid, alkylated (C8 - C20) phenoxyacetic acids, lanolin fatty acid and C8 - C24 mercapto-fatty acids.

Examples of Polybasic Carboxylic Acids

- 5 The alkenyl (C20 - C100) succinic acids indicated in CAS No. 27859-58-1 and ester derivatives thereof, dimer acid, N-acyl-N-alkyloxyalkyl aspartic acid esters (US-A-5,275,749) which have the structural formula indicated below and the compounds of CAS No. 68906-34-3.

10



- wherein R⁷ and R⁸ each independently represent hydrogen or a group selected from among the C1 to C30 alkyl groups, the C1 to C30 acyl groups and the alkyloxy groups, and R⁹ to R¹³ each independently represent hydrogen or a group selected from among the C1 to C30 alkyl groups.)
- 20

- Examples of the aforementioned alkylamines represented by general formula (1) include primary amines such as laurylamine, coconut-amine, n-tridecylamine, myristylamine, n-pentadecylamine, palmitylamine, n-heptadecylamine, stearylamine, n-nonadecylamine, n-eicosylamine, n-heneicosylamine, n-docosylamine, n-tricosylamine, n-pentacosylamine, oleylamine, beef tallow-amine, hydrogenated beef tallow-amine and soy bean-amine. Examples of the secondary amines include dilaurylamine, di-coconut-amine, di-n-tridecylamine, dimyristylamine, di-n-pentadecylamine, dipalmitylamine,
- 25
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di-n-pentadecylamine, distearylamine, di-n-nonadecylamine, di-n-eicosylamine, di-n-heneicosylamine, di-n-docosylamine, di-n-tricosylamine, di-n-pentacosylamine, dioleylamine, di-beef tallow-amine, di-
5 hydrogenated beef tallow-amine and di-soy bean-amine.

Examples of the aforementioned N-alkylpolyalkylenediamines which can be represented by general formula (2) include ethylenediamines such as laurylethylenediamine, coconut ethylenediamine, n-
10 tridecylethylenediamine, myristylethylenediamine, n-pentadecylethylenediamine, palmitylethylenediamine, n-heptadecylethylenediamine, stearylethylenediamine, n-nonadecylethylenediamine, n-eicosylethylenediamine, n-heneicosylethylenediamine, n-docosylethylendiamine, n-
15 tricosylethylenediamine, n-pentacosylethylenediamine, oleylethylenediamine, beef tallow-ethylenediamine, hydrogenated beef tallow-ethylenediamine and soy bean-ethylenediamine; propylenediamines such as laurylpropylenediamine, coconut propylenediamine, n-
20 tridecylpropylenediamine, myristylpropylenediamine, n-pentadecylpropylenediamine, palmitylpropylenediamine, n-heptadecylpropylenediamine, stearylpropylenediamine, n-nonadecylpropylenediamine, n-eicosylpropylenediamine, n-heneicosylpropylenediamine, n-docosylpropylendiamine, n-
25 tricosylpropylenediamine, n-pentacosylpropylenediamine, oleylpropylenediamine, beef tallow-propylenediamine, hydrogenated beef tallow-propylenediamine and soy bean-propylenediamine; butylenediamines such as laurylbutylenediamine, coconut butylenediamine,
30 n-tridecylbutylenediamine, myristylbutylenediamine, n-pentadecylbutylenediamine, stearylbutylenediamine, n-eicosylbutylenediamine, n-heneicosylbutylenediamine, n-docosylbutylendiamine, n-tricosylbutylenediamine, n-pentacosylbutylenediamine, oleylbutylenediamine, beef
35 tallow-butylenediamine, hydrogenated beef tallow-

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butylenediamine and soy bean butylenediamine; and
pentylenediamines such as laurylpentylenediamine, coconut
pentylenediamine, myristylpentylenediamine,
palmitylpentylenediamine, stearyl pentylenediamine, oleyl-
5 pentylenediamine, beef tallow-pentylenediamine,
hydrogenated beef tallow-pentylenediamine and soy bean
pentylenediamine.

In addition to the aforementioned components,
suitable amounts of supplementary additives of the
10 various types which are generally used can be added to
the lubricating oil composition of the present invention,
as required, in order to further improve the performance
thereof. Supplementary additives that may be added to
the lubricating oil composition of the present invention
15 include the known lubricating oil additives such as
antioxidants, metal deactivators, extreme pressure
additives, antifoaming agents, viscosity index increasing
agents, flow-point reducing agents, cleaning and
dispersing agents, anti-rust agents and anti-
20 emulsification agents.

Examples of amine-based antioxidants include
dialkyldiphenylamines such as p,p'-dioctyldiphenylamine
(manufactured by the Seiko Kagaku Co. under the trade
designation "Nonflex OD-3"), p,p'-di- α -
25 methylbenzyldiphenylamine and N-p-butylphenyl-N-p'-
octylphenylamine; monoalkyldiphenylamines such as mono-t-
butyldiphenylamine, and mono-octyldiphenylamine;
bis(dialkylphenyl)amines such as di(2,4-
diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine;
30 alkylphenyl-1-naphthylamines such as octylphenyl-1-
naphthylamine and N-t-dodecylphenyl-1-naphthylamine;
arylnaphthylamines such as 1-naphthylamine, phenyl-1-
naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-
naphthylamine and N-octylphenyl-2-naphthylamine,

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phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines such as phenothiazine (manufactured by the Hodogaya Kagaku Co.: Phenothiazine) and 3,7-dioctylphenothiazine.

Examples of sulphur-based antioxidants include dialkylsulphides such as didodecylsulphide and dioctadecylsulphide; thiodipropionic acid esters such as didodecyl thiodipropionate, dioctadecyl thiodipropionate, dimyristyl thiodipropionate and dodecyloctadecyl thiodipropionate, and 2-mercaptobenzimidazole.

Examples of phenol-based antioxidants include 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone (manufactured by the Kawaguchi Kagaku Co. under trade designation "Antage DBH"), 2,6-di-t-butylphenol and 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol; 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol, 3,5-di-t-butyl-4-hydroxybenzylmercaptooctyl acetate, alkyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionates such as n-octyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (manufactured by the Yoshitomi Seiyaku Co. under the trade designation "Yonox SS"), n-dodecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate; 2,6-di-t-butyl- α -dimethylamino-p-cresol, 2,2'-methylenebis(4-alkyl-6-t-butylphenol) compounds such as 2,2'-methylenebis(4-methyl-6-t-butylphenol) (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage W-400") and 2,2'-methylenebis(4-ethyl-6-t-butylphenol)

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(manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage W-500"); bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol) (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage W-300"), 4,4'-methylenebis(2,6-di-t-butylphenol) (manufactured by Laporte Performance Chemicals under the trade designation "Ionox 220AH"), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane (Bisphenol A), 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidenebis(2,6-di-t-butylphenol), hexamethylene glycol bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Irganox L109"), triethylene glycol bis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate] (manufactured by the Yoshitomi Seiyaku Co. under the trade designation "Tominox 917"), 2,2'-thio[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Irganox L115"), 3,9-bis{1,1-dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)-propionyloxy]ethyl}2,4,8,10-tetraoxaspiro[5,5]undecane (manufactured by the Sumitomo Kagaku Co. under the trade designation "Sumilizer GA80") and 4,4'-thiobis(3-methyl-6-t-butylphenol) (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage RC"), 2,2'-thiobis(4,6-di-t-butylresorcinol); polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionato]methane (manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Irganox L101"), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane (manufactured by the Yoshitomi Seiyaku Co. under the trade designation "Yoshinox 930"), 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene (manufactured by Ciba Speciality Chemicals under the trade designation "Irganox 1330"),

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bis[3,3'-bis(4'-hydroxy-3'-t-butylphenyl)butyric acid] glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl)-methyl-4-(2'',4''-di-t-butyl-3''-hydroxyphenyl)methyl-6-t-butylphenol and 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-4-methylphenol; and phenol/aldehyde condensates such as the condensates of p-t-butylphenol and formaldehyde and the condensates of p-t-butylphenol and acetaldehyde.

Examples of phosphorus-based antioxidants include triaryl phosphites such as triphenyl phosphite and tricresyl phosphite, trialkyl phosphites such as trioctadecyl phosphite and tridecyl phosphite, and tridodecyl trithiophosphite.

These antioxidants can be used individually or in the form of mixtures, conveniently in amounts within the range of from 0.01 to 2.0 parts by weight, per 100 parts by weight of base oil.

The metal deactivating agents which can be used in the lubricating oil a composition of the present invention include benzotriazole and the 4-alkylbenzotriazoles such as 4-methylbenzotriazole and 4-ethylbenzotriazole; 5-alkylbenzotriazoles such as 5-methylbenzotriazole, 5-ethylbenzotriazole; 1-alkylbenzotriazoles such as 1-dioctylaminomethyl-2,3-benzotriazole; benzotriazole derivatives such as the 1-alkyltolutriazoles, for example, 1-dioctylaminomethyl-2,3-tolutriazole; benzimidazole and benzimidazole derivatives such as 2-(alkyldithio)-benzimidazoles, for example, such as 2-(octyldithio)-benzimidazole, 2-(decyldithio)benzimidazole and 2-(dodecyldithio)-benzimidazole; 2-(alkyldithio)-toluimidazoles such as 2-(octyldithio)-toluimidazole, 2-(decyldithio)-toluimidazole and 2-(dodecyldithio)-toluimidazole; indazole and indazole derivatives of toluimidazoles such as 4-alkylindazole, 5-alkylindazole; benzothiazole, 2-

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mercaptobenzothiazole derivatives (manufactured by the Chiyoda Kagaku Co. under the trade designation "Thiolite B-3100") and 2-(alkyldithio)benzothiazoles such as 2-(hexyldithio)benzothiazole and

5 2-(octyldithio)benzothiazole; 2-(alkyldithio)toluthiazoles such as 2-(benzyldithio)toluthiazole and 2-(octyldithio)toluthiazole, 2-(N,N-dialkyldithiocarbamyl)benzothiazoles such as 2-(N,N-diethyldithiocarbamyl)benzothiazole, 2-(N,N-

10 dibutyldithiocarbamyl)benzotriazole and 2-N,N-dihexyldithiocarbamyl)benzotriazole; benzothiazole derivatives of 2-(N,N-dialkyldithiocarbamyl)toluthiazoles such as 2-(N,N-diethyldithiocarbamyl)toluthiazole, 2-(N,N-dibutyldithiocarbamyl)toluthiazole, 2-(N,N-dihexyldithiocarbamyl)toluthiazole;

15 2-(alkyldithio)benzoxazoles such as 2-(octyldithio)benzoxazole, 2-(decyldithio)benzoxazole and 2-(dodecyldithio)benzoxazole; benzoxazole derivatives of 2-(alkyldithio)toluoxazoles such as 2-(octyldithio)toluoxazole, 2-(decyldithio)toluoxazole,

20 2-(dodecyldithio)toluoxazole; 2,5-bis(alkyldithio)-1,3,4-thiadiazoles such as 2,5-bis(heptyldithio)-1,3,4-thiadiazole, 2,5-bis(nonyldithio)-1,3,4-thiadiazole, 2,5-bis(dodecyldithio)-1,3,4-thiadiazole and 2,5-bis(octadecyldithio)-1,3,4-thiadiazole; 2,5-bis(N,N-dialkyldithiocarbamyl)-1,3,4-thiadiazoles such as 2,5-bis(N,N-diethyldithiocarbamyl)-1,3,4-thiadiazole, 2,5-bis(N,N-dibutyldithiocarbamyl)-1,3,4-thiadiazole and 2,5-bis(N,N-dioctyldithiocarbamyl)-1,3,4-thiadiazole; thiadiazole derivatives of 2-N,N-dialkyldithiocarbamyl-5-mercapto-

25 1,3,4-thiadiazoles such as 2-N,N-dibutyldithiocarbamyl-5-mercapto-1,3,4-thiadiazole and 2-N,N-dioctyldithiocarbamyl-5-mercapto-1,3,4-thiadiazole, and triazole derivatives of 1-alkyl-2,4-triazoles such as 1-dioctylaminomethyl-2,4-triazole.

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These metal deactivating agents can be used individually or in the form of mixtures, conveniently in an amount within the range of from 0.01 to 0.5 parts by weight, per 100 parts by weight of base oil.

5 The materials which can be used as anti-foaming agents include, for example, dimethylpolysiloxane, organosilicates such as diethylsilicate, the fluorosilicones, and non-silicone based anti-foaming agents such as poly(alkylene acrylate). These can be
10 added and used individually or in the form of mixtures, conveniently in an amount of from 0.0001 to 0.1 part by weight, per 100 parts by weight of base oil.

 The viscosity index increasing agents which can be used include, for example, polymethacrylates and
15 ethylene/propylene copolymers, other non-dispersion type viscosity index increasing agents such as olefin copolymers like styrene/diene copolymers, and dispersible type viscosity index increasing agents where a nitrogen containing monomer has been copolymerized in such
20 materials. These materials can be added and used individually or in the form of mixtures, conveniently in an amount within the range of from 0.05 to 20 parts by weight per 100 parts by weight of base oil.

 Examples of flow-point reducing agents include
25 polymethacrylate based polymers. These materials can be added and conveniently used in an amount within the range from 0.01 to 5 parts by weight per 100 parts by weight of base oil.

 Examples of the cleaning and dispersing agents which
30 can be used include metal-based detergents such as the neutral and basic alkaline earth metal sulphonates, alkaline earth metal phenates and alkaline earth metal salicylates alkenylsuccinimide and alkenylsuccinimide esters and their borohydrides, and ashless dispersing
35 agents which have been modified with sulphur compounds.

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These agents can be added and used individually or in the form of mixtures, conveniently in an amount within the range of from 0.01 to 1 part by weight per 100 parts by weight of base oil.

5 Examples of extreme pressure additives include sulphur-based extreme pressure additives such as dialkyl sulphides, dibenzyl sulphide, dialkyl polysulphides, dibenzyl disulphide, alkyl mercaptans, dibenzothiophene and 2,2'-dithiobis(benzothiazole); phosphorus-based
10 extreme pressure additives such as trialkyl phosphates, triaryl phosphates, trialkyl phosphonates, trialkyl phosphites, triaryl phosphites and dialkylhydrozine phosphites, and phosphorus- and sulphur-based extreme pressure additives such as zinc dialkyldithiophosphates,
15 dialkylthiophosphoric acid, trialkyl thiophosphate esters, acidic thiophosphate esters and trialkyl trithiophosphates. These extreme pressure additives can be used individually or in the form of mixtures, conveniently in an amount within the range from 0.1 to 2
20 parts by weight, per 100 parts by weight of the base oil.

 The known anti-emulsifying agents which are generally used as lubricating oil additives can also be used. These agents may be conveniently added and used in an amount within the range from 0.0005 to 0.5 part by
25 weight, per 100 parts by weight of the base oil.

 Examples of anti-emulsifying agents include polyalkylene glycol-based non-ionic surfactants, for example, polyoxyethylenealkyl ethers, polyoxyethylene alkylphenyl ethers and polyoxyethylene alkylnaphthyl
30 ethers.

 The lubricating oil composition of the present invention is useful as a hydraulic oil composition, a compressor oil composition, a turbine oil composition, a bearing oil composition and/or a gear oil composition.

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The present invention will now be described with reference to the following Examples which are not intended to limit the scope of the present invention in any way.

5 Illustrative Examples

Sample oils were prepared by compounding extreme pressure additives and carboxylic acid based and carboxylic acid ester-based anti-rust agents and amines at various concentrations as shown in Table 1 in a hydrogenation refined base oil of kinematic viscosity 31 mm²/s at 40°C with a viscosity index of 107, a sulphur content of less than 5 ppm, a nitrogen content of less than 1 ppm and an aniline point of 112°C as the base oil.

15 The effect of the invention was investigated in terms of the anti-rust agent performance and the extreme pressure performance.

The test methods used for assessing performance in the Examples and Comparative Examples were as indicated below.

20 Anti-rust Test

In order to evaluate the anti-rust performance of the sample oils, an anti-rust test was carried out for 24 hours at 60°C in the presence of artificial seawater in accordance with ASTM D665. It was investigated whether or not rust had formed on the steel specimen after the test.

FZG Gear Wheel Test

30 In order to evaluate the lubrication performance of the sample oils in gear wheel equipment, the A test gear wheels were used in accordance with ISO/WD14635-1 and the gears were run for 15 minutes at each loading stage at an initial oil temperature of 90°C and a motor speed of 1450 rpm. The loading stage at which scorching occurred on

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the tooth surfaces of the test gear wheel as the load was being increased in stages was observed.

Examples 1 to 9 and Comparative Examples 1 to 9

5 The compositions and test results are shown in
Tables 1 to 3.

Table 1

Example/Comparative Example	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7
Base Oil, wt%	99.98	99.93	99.93	99.94	99.94	99.94	99.78
Extreme Pressure Additive, wt%							
3(O,O-diisobutyl-dithiophosphoryl)-2-methyl-propionic acid	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Triphenyl phosphothioate	-	-	-	-	-	-	-
Isobutyl acidic phosphate ester	-	-	-	-	-	-	-
Carboxylic Acid-, Carboxylic Acid Ester-Based							
Anti-rust Agent Component, wt%			0.05	-	-	-	-
Polyalkylene succinic acid half ester (1)	-	-	-	0.04	-	-	-
N-Oleyl sarcosinic acid (2)	-	-	-	-	0.04	-	-
Nonyl phenoxacetate (3)	-	-	-	-	-	0.04	-
N-Acyl-N-alkoxyalkyl aspartic acid ester A (4)	-	-	-	-	-	-	0.20
N-Acyl-N-alkoxyalkyl aspartic acid ester B (5)	-	-	-	-	-	-	-
Amine Component, wt%							
Coconut-amine	-	0.05	-	-	-	-	-
Oleylamine	-	-	-	-	-	-	-
Di-coconut-amine	-	-	-	-	-	-	-
Beef Tallow propylenediamine	-	-	-	-	-	-	-
Anti-rust Test Results	Rust formed >12	Rust Formed >12	No Rust 8	No Rust 8	No Rust 8	No Rust 9	No Rust 9
FZG Gear Wheel Test Results Minimum Failing Load Stage	>12	>12	8	8	8	9	9

Table 2

Example/Comparative Example	Comp. Ex. 8	Comp. Ex. 9	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Base Oil, wt%	99.53	99.35	99.95	99.955	99.95	99.955	99.88
Extreme Pressure Additive, wt%							
3(0,0-diisobutyl-dithiophosphoryl)-2-methyl- propionic acid	-	-	0.02	0.02	0.02	0.02	0.02
Triphenyl phosphothioate	0.50	0.50	-	-	-	-	-
Isobutyl acidic phosphate ester	0.10	0.10	-	-	-	-	-
Carboxylic Acid-, Carboxylic Acid Ester-Based Anti-rust Agent Component, wt%							
Polyalkylene succinic acid half ester (1)	-	-	0.01	-	-	-	-
N-Oleyl sarcosinic acid (2)	-	-	-	0.005	-	-	-
Nonyl phenoxacetate (3)	-	-	-	-	0.01	-	-
N-Acyl-N-alkoxyalkyl aspartic acid ester A (4)	0.05	-	-	-	-	0.005	-
N-Acyl-N-alkoxyalkyl aspartic acid ester B (5)	-	-	-	-	-	-	0.05
Amine Component, wt%							
Coconut-amine	-	0.05	0.02	0.02	0.02	0.02	0.05
Oleylamine	-	-	-	-	-	-	-
Di-coconut-amine	-	-	-	-	-	-	-
Beef Tallow propylenediamine	-	-	-	-	-	-	-
Anti-rust Test Results	No Rust	Rust Formed	No Rust	No Rust	No Rust	No Rust	No Rust
FZG Gear Wheel Test Results	9	>12	11	11	10	>12	11
Minimum Failing Load Stage							

Table 3

Example/Comparative Example	Example 6	Example 7	Example 8	Example 9
Base Oil, wt%	99.955	99.945	99.955	99.937
Extreme Pressure Additive, wt%				
3 (O,O-diisobutyl-dithiophosphoryl)-2-methylpropionic acid	0.02	0.02	0.02	-
Triphenyl phosphothioate	-	-	-	0.50
Isobutyl acidic phosphate ester	-	-	-	0.10
Carboxylic Acid-, Carboxylic Acid Ester-Based				
Anti-rust Agent Component, wt%				
Polyalkylene succinic acid half ester (1)	-	-	-	-
N-Oleyl sarcosinic acid (2)	-	-	-	-
Nonyl phenoxyacetate (3)	-	-	-	-
N-Acyl-N-alkoxyalkyl aspartic acid ester A (4)	0.005	0.005	0.005	0.01
N-Acyl-N-alkoxyalkyl aspartic acid ester B (5)	-	-	-	-
Amine Component, wt%				
Coconut-amine	-	-	-	0.02
Oleylamine	0.02	-	-	-
Di-coconut-amine	-	0.03	-	-
Beef Tallow propylenediamine	-	-	0.02	-
Anti-rust Test Results	No Rust	No Rust	No Rust	No Rust
FZG Gear Wheel Test Results	>12	>12	>12	>12
Minimum Failing Load Stage				

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NOTES:

1. manufactured by the Lubrizol Co under the trade designation "Lubrizol 859".
 2. manufactured by the Ciba Speciality Chemicals Co.
5 under the trade designation "Sarcosil O".
 3. manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Irgacore NPA".
 4. manufactured by the Colonial Chemical Co. under the trade designation "Korakoa 93".
 - 10 5. CAS No. 68906-34-3, 27136-73-8.
 6. manufactured by the King Industries Co. under the trade designation "K-CORR 100".
- Anti-rust agent disclosed in US-A-5,275,749.

Comparative Example 1 had only the extreme pressure
15 additive compounded therein. Whilst said example and exhibited good extreme pressure performance in the gear wheel test, rust formed in the anti-rust test as no anti-rust agent and amine had been added thereto.

In contrast, in Comparative Examples 3 to 8 the
20 minimum amount of carboxylic acid-based or carboxylic acid ester-based anti-rust agent had been added thereto and thus no rust formed in the anti-rust test. However, there was a marked fall in the durable load in the FZG gear wheel test as a result of the addition of the anti-rust agent.
25

Furthermore, only the amine had been added in Comparative Examples 2 and 9, with no carboxylic acid-based or carboxylic acid ester-based anti-rust agent also being added. Adequate anti-rust effect was not obtained.

30 With Examples 1 to 9, which are according to the present invention, the amount of carboxylic acid-based or carboxylic acid ester-based anti-rust agent required was greatly reduced as a result of the synergistic effect between the amine and the carboxylic acid-based or

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carboxylic acid ester-based anti-rust agent which are essential components of the invention, and there was a great improvement in respect of the fall in the extreme pressure performance which was caused by the anti-rust agent.

The lubricating oil compositions of the present invention are virtually free, or completely free, of metals which are harmful in respect of both the environment and safety and they maintain a good anti-rust performance whilst also having good extreme pressure performance to match the increased speeds, higher pressures, more compact nature and improvement in durability requirements of modern industrial machinery.

Furthermore, the amount of anti-rust agent added can be reduced by means of the present invention and lubricating oil compositions which have excellent performance can be provided more cheaply.

The lubricating oil compositions of the present invention are useful as lubricating oil compositions where both anti-rust performance and extreme pressure performance are required and they can be used as hydraulic working oils, gear wheel oils, compressor oils, turbine oils and bearing oils.

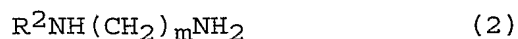
C L A I M S

1. Lubricating oil composition comprising a minor amount of an additive combination comprising
(i) a carboxylic acid-based or carboxylic acid ester-based anti-rust agent;

5 (ii) at least one type of amine selected from among the group comprising (A) the alkyl amines which can be represented by general formula (1),



10 wherein R^1 represents a saturated or unsaturated alkyl group which has from 12 to 30 carbon atoms, and n is an integer of value 1 or 2; and (B) the N-alkylpolyalkylenediamines which can be represented by general formula (2),



15 wherein R^2 represents a saturated or unsaturated alkyl group which has from 12 to 30 carbon atoms, and m is an integer of value from 2 to 5; and a major amount of lubricating oil base oil.

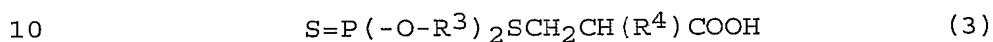
2. Lubricating oil composition according to Claim 1,
20 wherein said composition comprises from 0.001 to 0.5 part by weight of the carboxylic acid-based or carboxylic acid ester-based anti-rust agent; and from 0.001 to 0.2 part by weight of the at least one type of amine, per 100 parts by weight of lubricating oil base oil.

25 3. Lubricating oil composition according to Claim 1 or 2, wherein said composition comprises from 0.001 to 0.05 part by weight of the carboxylic acid-based or carboxylic acid ester-based anti-rust agent, per 100 parts by weight of lubricating oil base oil.

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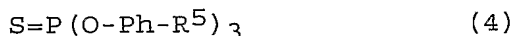
4. Lubricating oil composition according to any one of Claims 1 to 3, wherein said composition comprises from 0.001 to 0.05 part by weight of the at least one type of amine, per 100 parts by weight of lubricating oil base oil.

5. Lubricating oil composition according to any one of Claims 1 to 4, which further comprises, as an extreme pressure additive, a β -dithiophosphorylpropionic acid which can be represented by general formula (3),



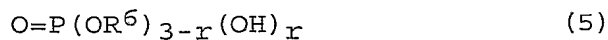
wherein R^3 represents a branched alkyl group which has from 3 to 8 carbon atoms, and R^4 is a hydrogen atom or a group selected from among the linear chain or branched alkyl groups which have from 1 to 4 carbon atoms.

6. Lubricating oil composition according to any one of Claims 1 to 5, which further comprises, as an extreme pressure additive, a triaryl phosphorothioate which can be represented by general formula (4)



wherein Ph represents a phenyl group, and R^5 is a hydrogen atom or a linear chain or branched alkyl group which has from 1 to 9 carbon atoms.

7. Lubricating oil composition according to any one of Claims 1 to 6, which further comprises, as an extreme pressure additive, an acidic phosphate ester which can be represented by general formula (5),



wherein R^6 is a linear chain or branched alkyl group which has from 3 to 13 carbon atoms, and r is an integer of value 1 or 2.

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8. Lubricating oil composition according to any one of Claims 1 to 7, wherein the lubricating oil base oil is a petroleum based and/or synthetic hydrocarbon based oil.

5 9. Lubricating oil composition according to Claim 8, wherein the lubricating oil base oil has a kinematic viscosity of from 2 to 680 mm²/s (40°C), a total sulphur content of from 0 to 1 wt. %, a total nitrogen content of from 0 to 100 ppm, and an aniline point of from 80 to 130°C.

10 10. Lubricating oil composition according to any one of Claims 1 to 9, which is used as a hydraulic oil composition, a compressor oil composition, a turbine oil composition, a bearing oil composition and/or a gear oil composition.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/05066

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10M141/00 //(C10M141/00, 129:36, 129:40, 129:58, 129:76, 133:06, 135:26, 137:02, 137:04, 137:10), C10N30:12, C10N40:02, C10N40:04, C10N40:12, C10N40:30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 744 456 A (ETHYL PETROLEUM ADDITIVES LTD) 27 November 1996 (1996-11-27) page 15, line 34 - line 58; claims 1-12 page 7, line 5 - line 45 ----	1-3, 8, 10
X	US 5 152 908 A (TIPTON CRAIG D) 6 October 1992 (1992-10-06) column 5, line 40 - column 7, line 25; claims 1-3; examples 1, 3 ----	1, 2, 8, 10
X	WO 00 11122 A (BABA YOSHIHARU ; HANYUDA KIYOSHI (JP); SHELL INT RESEARCH (NL)) 2 March 2000 (2000-03-02) page 3, line 11 - page 5, line 5; claims 1, 2; tables 1, 4 ----- -/--	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

27 September 2002

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/05066

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 819 754 A (CIBA GEIGY AG) 21 January 1998 (1998-01-21) page 9; claim 1 -----	1-10
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 02, 26 February 1999 (1999-02-26) & JP 10 298575 A (COSMO SOGO KENKYUSHO:KK;COSMO OIL CO LTD), 10 November 1998 (1998-11-10) abstract -----	1-10

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International Application No

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